Modeling and Analysis of Oxidation and Thermal Stability of Biodiesel

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Abstract-**The present paper reports the model developed for the oxidation and thermal stability as a function of metal contaminants and antioxidant concentration using Response Surface Methodology (RSM). Taking Pyrogallol (PY) as the most effective antioxidant based on the earlier work of the authors, Jatropha curcas biodiesel (JCB) was mixed with different transition metals – Fe, Ni, Mn, Co and Cu in different concentrations. Induction period (IP) was measured using Rancimat method (EN 14112). The ASTM D6468 and TGA methods are used for evaluating the thermal behavior of JCB. Based on results, several correlations are developed for assessing the thermal stability in terms of Insoluble formation (Ins) and activation energy (E_a) as a function of antioxidant and metal concentration. For the purpose of design of experiment, RSM has been used. A comparison between the experimental values and those predicted by the correlation shows that all the data points lie within ±10% deviation lines of the experimental results. The models developed by response surface methodology (RSM) shall be highly useful for predicting the optimum antioxidant concentration to impart maximum fuel stability to JCB. Also the correlations developed in the present paper are useful for the development of specification for thermal stability of biodiesel.**

Keywords-Jatropha curcas biodiesel, oxidation stability, thermal stability.

I. INTRODUCTION

Biodiesel is defined as the monoalkyl ester obtained from the transesterification of agricultural lipids such as vegetable oil, animal fats etc [1]. The fatty acid profile of biodiesel resembles the parent oil or fat and is the major factor influencing its fuel properties. Due to the presence of significant amount of fatty acids with double bonds, the fuel quality in terms of oxidative stability of biodiesel is found to be of serious concern when it is stored over an extended period of time. The storage problems can be caused by storage conditions like exposure to air and/or light, temperature as well as the presence of metals with catalytic effect on oxidation. This fuel instability can give rise to sediments and gum formation and fuel darkening. The biodiesel and its blends are found to be more prone to oxidation than the straight vegetable oils (SVO) and can form wide variety of alcohols, aldehydes, peroxide, insoluble gum, sediments, etc. during its transport and long-term storage, thereby, causing acidity in the fuel [1-4]. The use of such degraded biofuel in engine causes operational problems like fuel filter plugging, injector fouling, deposit formation in engine combustion chamber and various other components of the fuel delivery system, thus, affecting the engine performance badly. This instability of fuel quality can be characterized by the indicators like formation of color, presence of soluble gums and insolubles in the fuel which are the important stability characteristics. Stability of biodiesel may be affected by its interaction with contaminants, light, temperature, factors causing sediments formation, changes in color and other changes that reduce the cleanliness of the fuel [2- 4].

At sufficiently high temperatures, the methylene-interrupted polyunsaturated olefin structure will begin to isomerize to form more stable conjugated structure. Once this isomerization has initiated, a conjugated diene group from one fatty acid chain can react with a single olefinic group from another fatty acid chain to form a cyclohexene ring. The reaction between a conjugated di-olefin and a mono-olefin group, called Diels Alder reaction which becomes important at temperatures of 250°-300°C or more and the reaction products formed are called dimmers [1- 7].

Mittelbach and Schober [8] have studied the influence of antioxidants on the oxidation stability of biodiesel and showed the influence of different synthetic and natural antioxidants on the oxidation stability using the specified test method. Dunn et al. [9] examined the effectiveness of five such antioxidants as tert-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PrG) and α-tocopherol in mixtures with soybean oil fatty acid methyl esters (SME) and found that increasing antioxidant loading (concentration) increases the activity also. Sarin et al. [10] have worked on Jatropha curcas biodiesel (JCB) and found out an optimum mix for Asia using different blends of palm and Jatropha curcas biodiesel having improved oxidation stability. Liang et al. [11] have examined the effect of natural and synthetic antioxidants on the oxidative stability of palm biodiesel and found that crude palm oil methyl ester (CPOME) containing about 600 ppm of vitamin E exhibited oxidative stability of more than 6 h which conforms to the specification of the European standard for biodiesel (EN 14214).

Some workers have further evaluated the influence of metal contaminants on oxidation stability of JCB [12 and 13] and experimentally, it was found that influence of metals was detrimental to the oxidation stability. Even small concentrations of metal contaminants showed nearly the same influence on oxidation stability as shown by high concentration. Cu showed strongest detrimental and catalytic effect (fig 1). Fritsch et al. [14] have examined the effect of antioxidants on

refined palm oil and found TBHQ to have better effect as antioxidant on refined palm oil than BHT and BHA.

The above literature reveals that biodiesel is more prone to oxidation and thermal degradation when it is in contact with metal contaminants. However this problem can be solved by adding antioxidants. Based on the available literature reports, it is prudent to carryout extensive experiment to analyze the effect of contamination on thermal and oxidation stability of biodiesel. RSM approach of design of experiments (DOE) is one of the emerging techniques, which helps in carrying out the analysis of experiments with the least experimental effort [15].

Therefore the aim of the present paper is to do modeling and analysis of thermal and oxidation stability of biodiesel. For the purpose of design of experiments, response surface methodology (RSM) methodology has been used using design expert 8.0 software. There are various methods available for the measurement of thermal stability of biodiesel as already discussed by Jain and Sharma [5]. In the present paper ASTM D6468-08 and TGA is used for the measurement of thermal stability and EN 14112 is used for the measurement of oxidation stability of biodiesel [16, 17].

II. MATERIAL

The biodiesel used in the experiments was prepared using 2 step acid base catalyzed transesterification processes as reported in our previous paper [18, 19]. Physico chemical properties of JCB are shown in table 1. Different transition metals – Fe, Ni, Mn, Co and Cu have also been purchased from Sigma Aldrich, India. Pyrogallol (PY) was the additives employed for evaluating its effect on the stability of biodiesel.

III. METHODS

The effectiveness of various antioxidants has already been checked and reported in our previous publication [20]. It was found that PY is the most effective antioxidant used to increase the oxidation stability of JCB. PY is mixed in different concentrations in metal contaminated biodiesel. The oxidation stability was measured using EN 14112 and thermal stability is measured using ASTM D6468-08 and TGA. The descriptions of test methods are given in our earlier publications [16, 17].

IV. DESIGN OF EXPERIMENTAL

Response Surface Methodology (RSM) has been used to investigate the influence of metal contaminants and antioxidant concentration on the oxidation stability of biodiesel in terms of induction period. A 5-level-2-factor central composite design (CCD) including 2 replicates at factorial, 2 replicates at axial and 5 replicates at the centre point leading to 21 runs, was used for fitting the response surface.

Metal contaminants and antioxidant concentration were the independent variables selected to be optimized for obtaining the 6 hrs induction period of JCB. The coded and uncoded levels of the independent variables are given in table 2.

The experimental data obtained by following the above procedures were analyzed by the response surface regression procedure using the following second-order polynomial equation:

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \qquad (1)$$

Where y is the response (induction period); xi and xj are the uncoded independent variables and β0, βi, βii and βij are intercept, linear, quadratic and interaction constant coefficients, respectively. Design Expert software package 8.0 was used for regression analysis and analysis of variance (ANOVA). Several optimization points for each independent variable at which an induction period of 6 hrs, were obtained. Confirmatory experiments were carried out to validate the equations, using combinations of independent variables, which were not part of the original experimental design but were within the experimental region.

TABLE I. PHYSICO- CHEMICAL PROPERTIES OF BIODIESEL AS PER DIFFERENT STANDARDS

S.No.	Property (unit)	ASTM D6751	ASTM D6751 limits	Jatropha ME
1	Flash point(^{0}C)	D-93	Min.130	172
2	Viscosity at 40^{0}C(cSt)	D-445	1.9-6.0	4.38
3	Water and sediment (vol%)	D-2709	Max.0.05	0.05
4	Free glycerin (% mass)	D-6584	Max.0.02	0.01
5	Total glycerin (% mass)	D-6584	Max.0.24	0.03
6	Oxidation stability of FAME, hrs	EN14112	3	3.27
7	Oxidation stability of FAME blend, hrs	-	-	-
8	Free glycerol	D6584	0.02 (max)	0.01
9	Total glycerol	D6584	0.25(max)	0.12
10	Acid value	D664	0.5(max)	0.38
11	Ester content	-	-	98.5

TABLE II: INDEPENDENT VARIABLE AND LEVELS USED FOR CCD IN OXIDATION PROCESS FOR ALL THE METALS

Variables	Symbols	Levels				
		-1.68179 (-α)	*-1*	*0*	*+1*	*+1.68179 (+α)*
Antioxidants concentration (ppm)	A	0	150	300	450	600
Metal contaminants concentration (mg/L)	M	0	0.5	1	1.5	2

V. RESULTS AND DISCUSSION

A. Response analysis of Fe Contaminated Biodiesel

Experimental as well as predicted values obtained for induction period responses of Fe contaminated biodiesel at the

design points are shown in table 3. Both the variables are shown in both coded and uncoded (actual) form.

The application of RSM yields the following regression equations which are empirical relationship for thermal and oxidation stability in terms of antioxidant concentration and metal concentration.

$$IP = 3.52+0.030528*A-1.84833*M-5.66667*10^{-3}*A*M-7.19444*10^{-6}*A^2+0.16750*M^2 \quad (2)$$

$$Ins = 0.57091-7.13131*10^{-4}*A+0.16273*M-2.33333*10^{-4}*A*M+5.68182*10^{-7}*A^2+6.13636*10^{-3}*M^2 \quad (3)$$

$$E_a = 43.67848+0.090157*A-10.73288*M+5.23333*10^{-3}*A*M-5.99192*10^{-5}*A^2-0.42273*M^2 \quad (4)$$

Equation 2 is plotted in figure 1 as response surface plots of oxidation stability in terms of IP. This figure shows that the IP improves with increase of antioxidant concentration at constant amount of metal contaminants.

TABLE III. CCD ARRANGEMENT AND RESPONSES FOR OXIDATION PROCESS OF FE CONTAMINATED JCB

Treatment	Random	Level of variables [(coded) actual]		Induction period (hrs)		Insoluble formation		Activation energy	
		Antioxidant, A (ppm)	*Metal conc, M (mg/L)*	*Exp.*	*Predicted*	*Exp.*	*Predicted*	*Exp.*	*Predicted*
1	4	(-1)150	(-1)0.5	6.25	6.63	0.49	0.54	51.35	50.77
2	16	(-1)150	(-1)0.5	6.55	6.63	0.55	0.54	55.29	50.77
3	3	(+1)450	(-1)0.5	13.2	13.64	0.37	0.39	65.95	67.82
4	20	(+1)450	(-1)0.5	13.6	13.64	0.41	0.39	69.33	67.82
5	13	(-1)150	(+1)1.5	4.25	4.27	0.66	0.68	41.12	39.98
6	14	(-1)150	(+1)1.5	4.55	4.27	0.7	0.68	43.84	39.98
7	9	(+1)450	(+1)1.5	9.5	9.58	0.45	0.46	56.85	58.59
8	15	(+1)450	(+1)1.5	9.9	9.58	0.51	0.46	59.89	58.59
9	5	(-α)0	(0)1	1.76	1.84	0.73	0.73	28.96	32.52
10	18	(-α)0	(0)1	1.96	1.84	0.77	0.73	32.2	32.52
11	10	(+α)600	(0)1	13.96	14.17	0.35	0.37	66.45	68.18
12	21	(+α)600	(0)1	14.44	14.17	0.39	0.37	71.49	68.18
13	8	(0)300	(-α)0	11.96	12.03	0.41	0.40	62.32	65.33
14	2	(0)300	(-α)0	12.52	12.03	0.43	0.40	67.14	65.33
15	11	(0)300	(+α)2	5.25	5.60	0.6	0.61	43.12	45.31
16	12	(0)300	(+α)2	5.65	5.60	0.62	0.61	46.4	45.31
17	17	(0)300	(0)1	8.5	8.65	0.52	0.50	52.45	55.74
18	19	(0)300	(0)1	8.75	8.65	0.54	0.50	57.19	55.74
19	7	(0)300	(0)1	8.7	8.65	0.5	0.50	53.42	55.74
20	6	(0)300	(0)1	8.62	8.65	0.48	0.50	56.22	55.74
21	1	(0)300	(0)1	8.9	8.65	0.51	0.50	54.82	55.74

*Exp. stands for experimental, Conc. stands for concentration

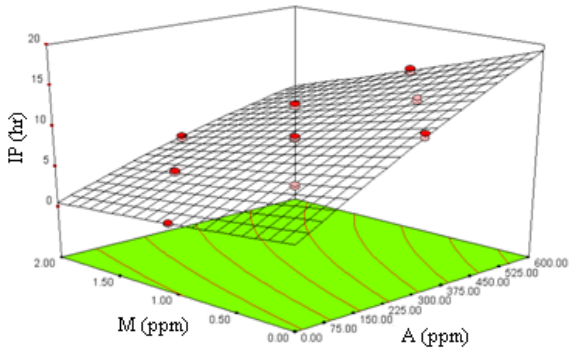

Figure 1. The response surface plot of the IP for JCB

Figure 2 depicts response surface plots represented by Equation 3 for thermal stability in terms of Ins. Similarly, this figure reveals that the Ins decreases with increase in antioxidant concentration at constant amount of metal contaminants.

Equation 4 is plotted in figure 3 as response surface plots for thermal stability in terms of Ea. Clearly, this figure confirms that the Ea increases with the increasing amount of antioxidant concentration at constant metal concentration.

In the same manner, the response analysis of other metal contaminated biodiesel is conducted. The model developed for IP, Ins and Ea for all the metals selected for experiment are given in table 4. Experimental as well as predicted values obtained for IP, Ins and Ea responses of other metal contaminated biodiesel at the design points are shown in figure 4, 5 and 6 respectively from which it is clear that maximum error of ±10% is existing between experimental and predicted values of IP from CCD generated model. Table 5 is showing the summery of ANOVA for all the metal contaminated biodiesel.

For all the models, F- value is large enough to make the model significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. In all cases A, M, AM, A2, M2 are significant model terms. Also lack of fit is not significant which is desirable. Predicted R2 value is in reasonable agreement with adjusted R2 value.

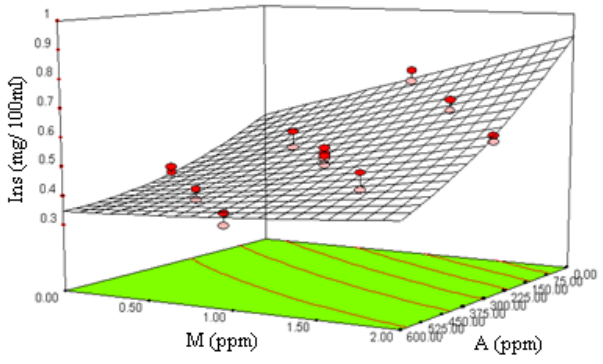

Figure 2. The response surface plot of the Ins for JCB

TABLE IV. PREDICTED MODELS FOR IP, Ins AND Ea

S. No.	Metal	Predicted model
1	Fe	IP=3.52+0.030528*A-1.84833*M-5.66667*10^{-3}*A*M-7.19444*10^{-6}*A^2+0.16750*M^2 Ins=0.57091-7.13131*10^{-4}*A+0.16273*M-2.33333*10^{-4}*A*M+5.68182*10^{-7}*A^2+6.13636*10^{-3}*M^2 E_a=43.67848+0.090157*A-10.73288*M+5.23333*10^{-3}*A*M-5.99192*10^{-5}*A^2-0.42273*M^2
2	Ni	IP=4.05394+0.028184*A-3.09152*M-6.33333*10^{-3}*A*MC-4.73232*10^{-6}*A^2+0.78409*M^2 Ins=0.59788-7.93434*10^{-4}*A+0.25197*M-2.66667*10^{-4}*A*M+6.18687*10^{-7}*A^2-0.019318*M^2 E_a=46.68424+0.079609*A-26.89727*M+0.026567*A*M-7096*10^{-5}*A^2+2.60114*M^2
3	Mn	IP=4.41515+0.025763*A-4.36455*M-6.33333*10^{-3}*A*M-7.52525*10^{-7}*A^2+1.34227*M^2 Ins=0.60152-8.07071*10^{-4}*A+0.28455*M-3.0*10^{-4}*A*M+6.69192*10^{-7}*A^2-0.024773*M^2 E_a=45.48939+0.083027*A-29.82515*M+0.027333*A*M-6.52121*10^{-5}*A^2+3.33091*M^2
4	Co	IP=4.12273+0.026438*A-4.34848*M-8.0*10^{-3}*A*M+2.32323*10^{-7}*A^2+1.40091*M^2 Ins=0.65182-9.98485*10^{-4}*A+0.33379*M-2.66667*10^{-4}*A*M+8.30808*10^{-7}*A^2-0.040227*M^2 E_a=43.21061+0.089323*A-36.88318*M+0.029667*A*M-6.90379*10^{-5}*A^2+5.31159*M^2
5	Cu	IP=3.70909+0.029541*A-3.82439*M-8.66667*10^{-3}*A*M-5.17929*10^{-6}*A^2+0.95886*M^2 Ins=0.63394-8.55051*10^{-4}*A+0.51015*M-4.0*10^{-4}*A*M+6.28788*10^{-7}*A^2-0.098409*M^2 E_a=40.33848+0.097579*A-45.83288*M+0.031867*A*M-7.48359*10^{-5}*A^2+8.00977*M^2

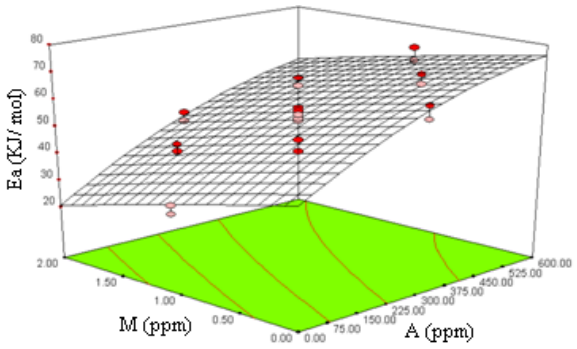

Figure 3. The response surface plot of the Ea for JCB

B. *Comparision between Statistical and RSM Results*

The authors used the stastical aproach for presdicting the oxidation and thermal stability of JCB in their previous publication [13 and 16]. Further a comparision between the correlations developed earlier using stastical technique and using RSM is conducted to check the validity of the model developed in the current paper.

Figure 7 and 8 shows that the coparision between the statistical correlations and RSM based correlations for Ins and Ea as a thermal stability parameter respectively. Fig also shows that the maximum error between both the correlation is ±10%.

Figure 9 shows the comparision between the statistical correlations and RSM based correlations for IP as a oxidation stability parameter. This fig is also showing the maximum error between both the correlation is ±10%.

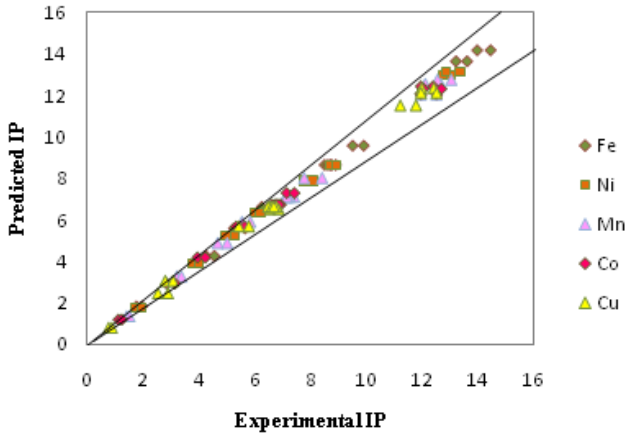

Figure 4. Comparision of experimental and predicted values of IP

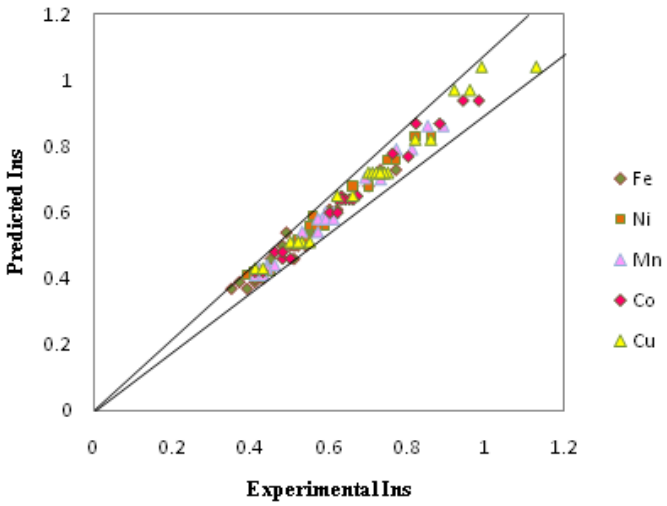

Figure 5. Comparision of experimental and predicted values of Ins

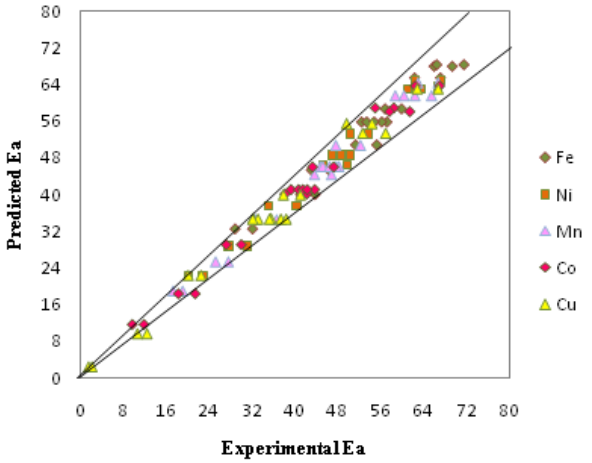

Figure 6. Comparision of experimental and predicted values of Ea

TABLE V. SUMMARY OF ANOVA

S. No.	Metal in biodiesel sample	Model F-value			Adjusted R^2			Predicted R^2		
		IP	*Ins*	E_a	*IP*	*Ins*	E_a	*IP*	*Ins*	E_a
1	Fe	765.75	71.76	69.31	0.9948	0.9465	0.9447	0.9914	0.9213	0.9120
2	Ni	952.28	171.11	142.41	0.9958	0.9770	0.9725	0.9928	0.9627	0.9539
3	Mn	746.96	212.87	169.80	0.9947	0.9815	0.9769	0.9915	0.9707	0.9622
4	Co	872	171.49	186.59	0.9954	0.9771	0.9789	0.9923	0.9642	0.9667
5	Cu	902.34	104.87	171.38	0.9956	0.9629	0.9771	0.9926	0.9335	0.9660

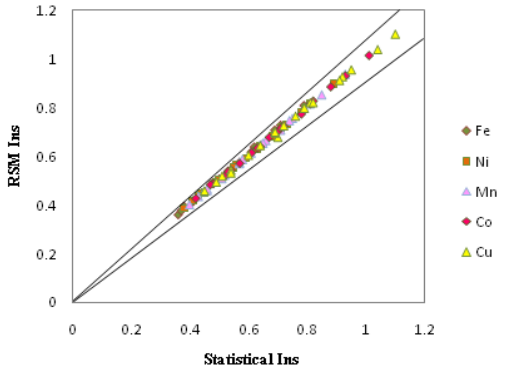

Figure 7. Comparision of statistical and RSM value of Ins

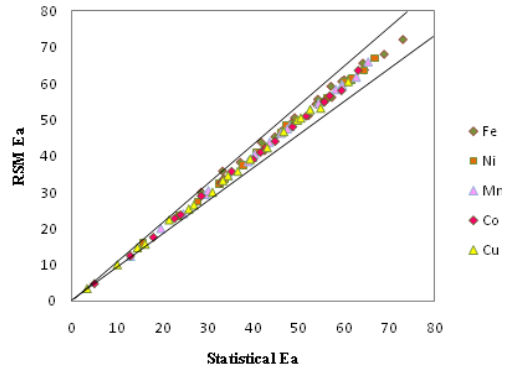

Figure 8. Comparision of statistical and RSM value of Ea

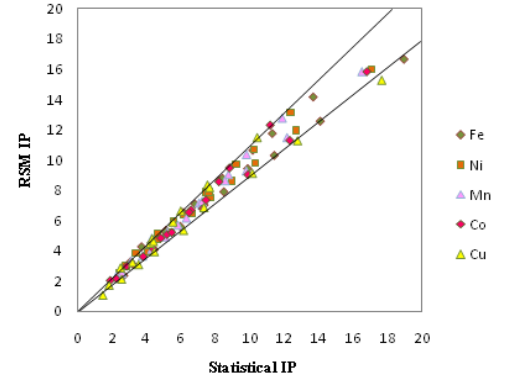

Figure 9. Comparision of statistical and RSM value of IP

The above results are showing that the RSM technique can be used for the modeling of thermal and oxidation stability. Using RSM techniqe one can reduce the number of experiments with no reduction in the accuracy of the results. now the amout of antioxidant can be optimised to get the IP of 6 hrs and accordingly one can calculate the Ins and Ea for the same IP. Since there is no specification for thermal stability the present correlations can be useful for development of specification for thermal stability of biodiesel.

VI. CONCLUSIONS

In the present paper the effect of antioxidant and metal contaminants on oxidation and thermal stability of biodiesel has been studied and based on the results a model is developed using RSM. A comparison between the IP, Ins and Ea obtained from experimental investigation and those predicted by the model developed shows that all the predicted data points lie within ±10% deviation lines of the experimental results. The models developed by RSM shall be highly useful for predicting the optimum antioxidant concentration to impart maximum fuel stability for biodiesel. The correlations developed can be used to predict the amount of antioxidants required to maintain the specification of 6 hr induction period for metal contaminated JCB with reasonable accuracy in the range of parameters investigated. And accordingly one can calculate the Ins and Ea for the same IP. Since there is no specification for thermal stability the present correlations can be useful for development of specification for thermal stability of biodiesel.

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